Advanced Thermoelectric Materials for Radioisotope Thermoelectric Generators

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Thierry Caillat

co-authors

C. -K. Huang, B. Cheng, S. C. Chi, P. Gogna, J. Paik, V. Ravi, S. Firdosy, and R. Ewell

Jet Propulsion Laboratory/California Institute of Technology

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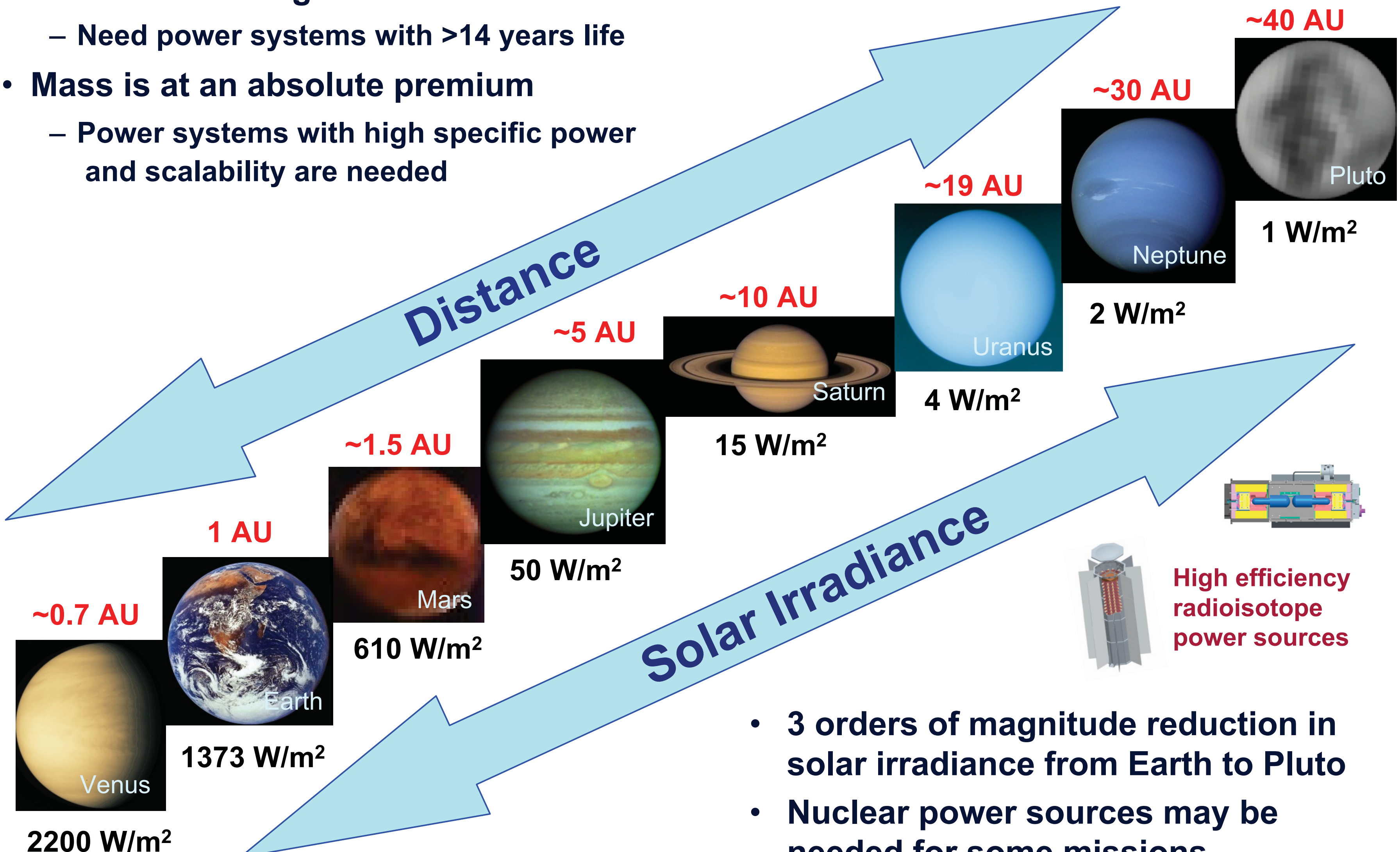
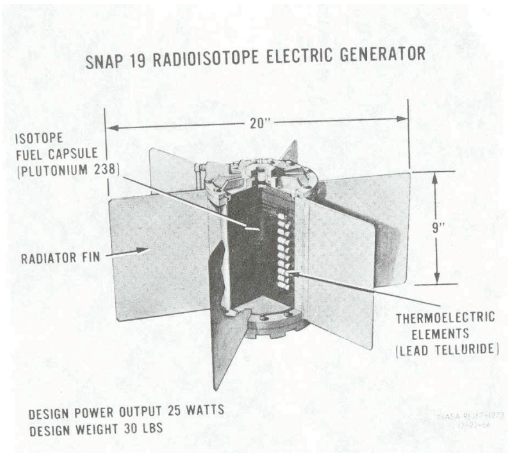
Space Power Technology

- Missions are long
  - Need power systems with >14 years life
- Mass is at an absolute premium
  - Power systems with high specific power and scalability are needed



- 3 orders of magnitude reduction in solar irradiance from Earth to Pluto
- Nuclear power sources may be needed for some missions

Flight Demonstrated
Radioisotope Thermoelectric Generators RTGs)
(3 Most Recently Flown Designs)

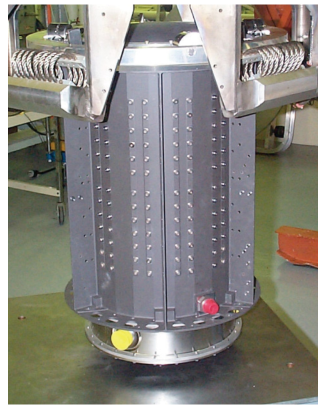


SNAP-19 (PbTe RTG)
(1960-70's)

40.3 Watts (Beginning of Mission)
6.2 % system efficiency
3 We/kg

22.86 cm (9.0 in) long
50.8 cm (20 in) diameter
~13 kg (28.6 lb)
PbTe Thermoelectrics

Nimbus B-1/III, Pioneer 10/11, Viking 1/2

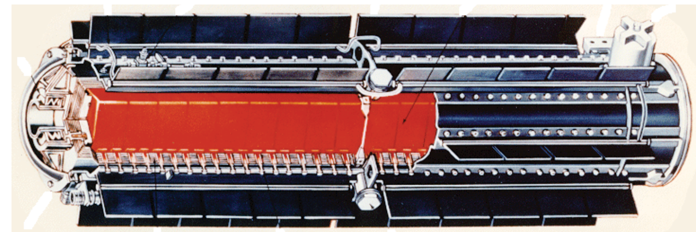


SiGe MHW RTG
(1970's)

158 We (Beginning of Mission)
6.6 % system efficiency
4.2 We/kg

58.4 cm (23 in) long
39.7 cm (15.64 in) diameter
38 kg (83.7lb)
SiGe Thermoelectrics

LES 8/9, Voyager 1/2



SiGe GPHS RTG
(1980-2006)

285 We (Beginning of Mission)
6.8% system efficiency
5.1 We/kg

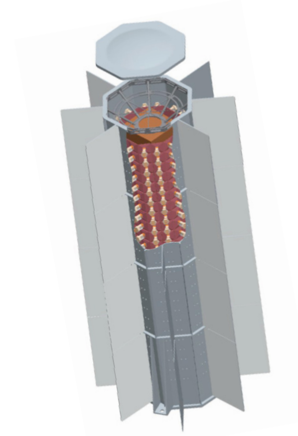
114 cm (44.9 in) long
42.7cm (16.8in) diameter
56 kg (123 lb)
SiGe Thermoelectrics

Galileo, Ulysses, Cassini & New Horizons

NASA Proposed Advanced RTG Needs

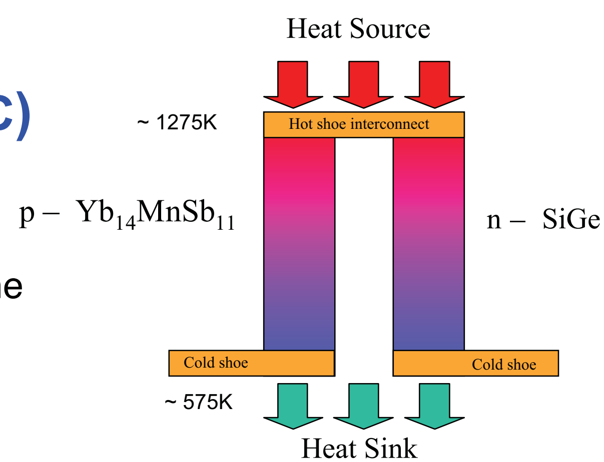
	Near Term	Long Term
Specific Power (W/kg)	6 - 8	> 10
Readiness	2015 - 2016	> 2020
Lifetime	> 14 years < 22% degradation	> 14 years < 22% degradation
Heat Source	Step 2 GPHS (8 to 12 units)	Step 2 GPHS (1 to 12 units)
System Efficiency (%)	8-10	13 - 15

- **Advanced RTGs**
  - Would require use of advanced TE materials to achieve higher efficiency
  - Advanced design to improve thermal efficiency



ARTG Conceptual Design

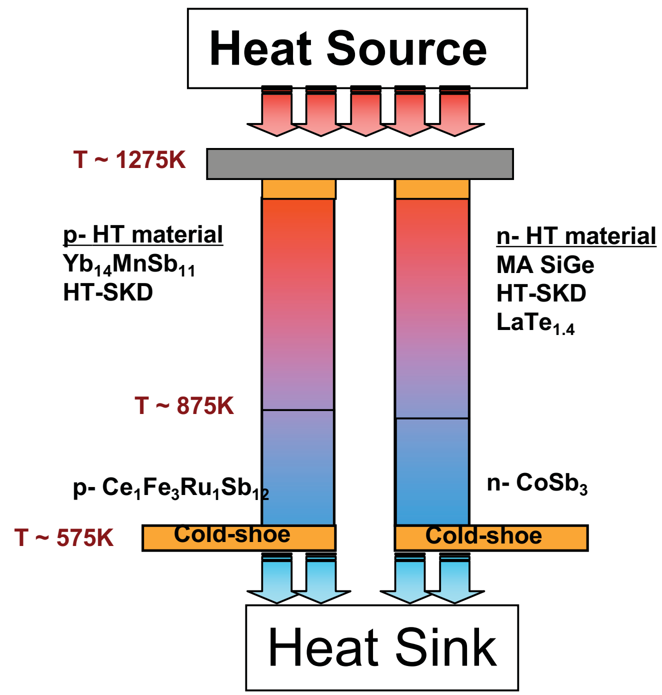
- **Advanced Thermoelectric Converter Project (ATEC)**
  - Developed ARTG Conceptual designs
    - Unsegmented unicouple chosen
    - Vacuum only design similar to GPHS-RTG selected as baseline
    - 6-8 W/kg
    - 8-10 % system efficiency



ATEC Primary unicouple configuration

ATEC Thermoelectric Materials Background

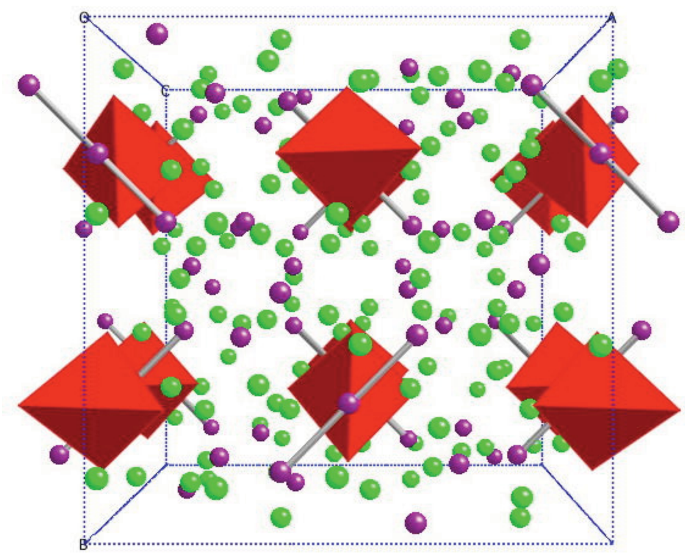
- **TE materials initially evaluated under ATEC**
  - **P-type**
    - $Yb_{14}MnSb_{11}$ (Zintl)
    - HT-Skutterudite: $Ce_yRu_{1-x}Fe_xSb_{12}$
    - $CeFe_3Ru_1Sb_{12}$
    - Nanostructured SiGe
  - **N-type**
    - Mechanically alloyed SiGe
    - $LaTe_{1.4}$
    - $CoSb_3$
    - HT-Skutterudite: $Co_xIr_{1-x}Sb_3$



- **TE materials requirements**
  - Must be phase stable at maximum operating temperature
  - Can be produced by a synthesis process that is scalable
  - Must have repeatable thermoelectric properties

Zintl Compounds for Thermoelectric Applications

- **$A_{14}MSb_{11}$ Zintl compounds**
  - A: Ca, Sr, Yb, Eu …
  - M: Al, In, Ga, Mn, Zn …
  - Many opportunities for doping and disorder
  - High decomposition temperatures >1275K
- **$Yb_{14}MnSb_{11}$**
  - High ZT reported[1]
    - Samples prepared by a flux method, milled, and hot-pressed
    - ZT ~1 at 1223K
  - Decomposition temperature > 1275K
- **$Ca_{14}AlSb_{11}$**
  - Ca^{2+} and Al^{3+}
  - Electron balanced
- **$Yb_{14}MnSb_{11}$**
  - XPS -> Yb^{2+} but Mn^{2+}
  - Electron deficient -> p-type behavior expected

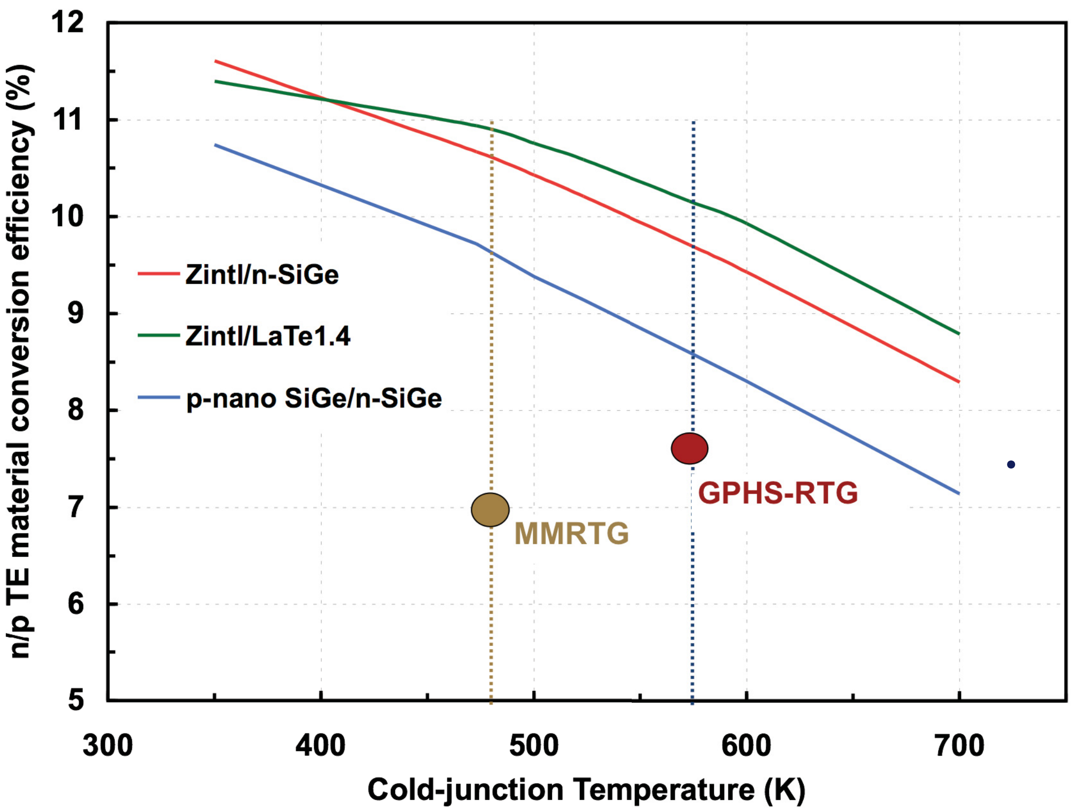


[1] **S. Brown *et al.*, *Chem. Mat.*, 18, 1873 (2006)**

Thermoelectric materials development status

Status		Decomposition temperature (K)	ZT_{ave} (1275 K - 575K)	TE properties repeatability demonstrated	Scaled-up synthesis process (100 g batch)
Primary p-type	P-Zintl ($Yb_{14}MnSb_{11}$)	≥ 1523	0.81	Yes	Developed
Back-up p-type	P-nano SiGe	~ 1553	0.56	Yes	Feasibility demonstrated
	P-low T SKD	~ 1050K	-	Yes	Developed
	P-high T SKD	≥ 1275K	-	No	Not developed
Primary n-type	N- SiGe	~1553	0.75	Yes	Developed
Back-up n-type	N-$LaTe_{1.4}$	≥ 1523	0.88	No	Feasibility demonstrated
	N-low T SKD	~ 1050K	-	Yes	Developed
	P-high T SKD	≥ 1275K	-	No	Not developed

Couple configuration options selected



- **Preliminary ARTG conceptual system design and performance studies**
  - Conducted by DOE contractors
  - Showed that several high-T materials combination can yield system efficiency ~ 10% and specific power greater than 6 W/kg
  - Segmenting high-T materials to low-temperature skutterudite materials does not provide substantial increase in efficiency (~0.5%) but adds development risk
  - Segmented configuration (with skutterudites) was not retained for further development
- **High-T couple configurations selected for development :**
  - Primary
    - P-type $Yb_{14}MnSb_{11}$ (Zintl)
    - N-type mechanically alloyed SiGe
  - Back-ups
    - N-$LaTe_{1.4}$
    - P-type $Yb_{14}MnSb_{11}$ (Zintl)
    - N-type mechanically alloyed SiGe
    - P-nano SiGe

TE materials synthesis

- **Power metallurgy synthesis**
  - Melting of elements up to ~ 1475 K in various crucibles under vacuum
  - Various post-anneal and milling steps
  - Milling in steel or WC under inert atmosphere
  - End product: powder

- **Planetary ball milling**
  - Vial load capacity: up to 250 g
  - Steel vials and balls
  - End product: powder

- **Vibratory ball milling**
  - Vial load capacity 10 – 15g
  - WC or steel vials and balls
  - End product: powder

TE property measurements

- Electrical resistivity (ρ) - up to ~ 1375 K
  - Van der Pauw
  - ~ 1 mm thick x 12 mm diameter disk
  - Error ~ 2%
- Seebeck coefficient (α) - up to ~ 1375 K
  - Small gradient technique
  - ~ 1 mm thick x 12 mm diameter disk
  - Error ~ 5 %

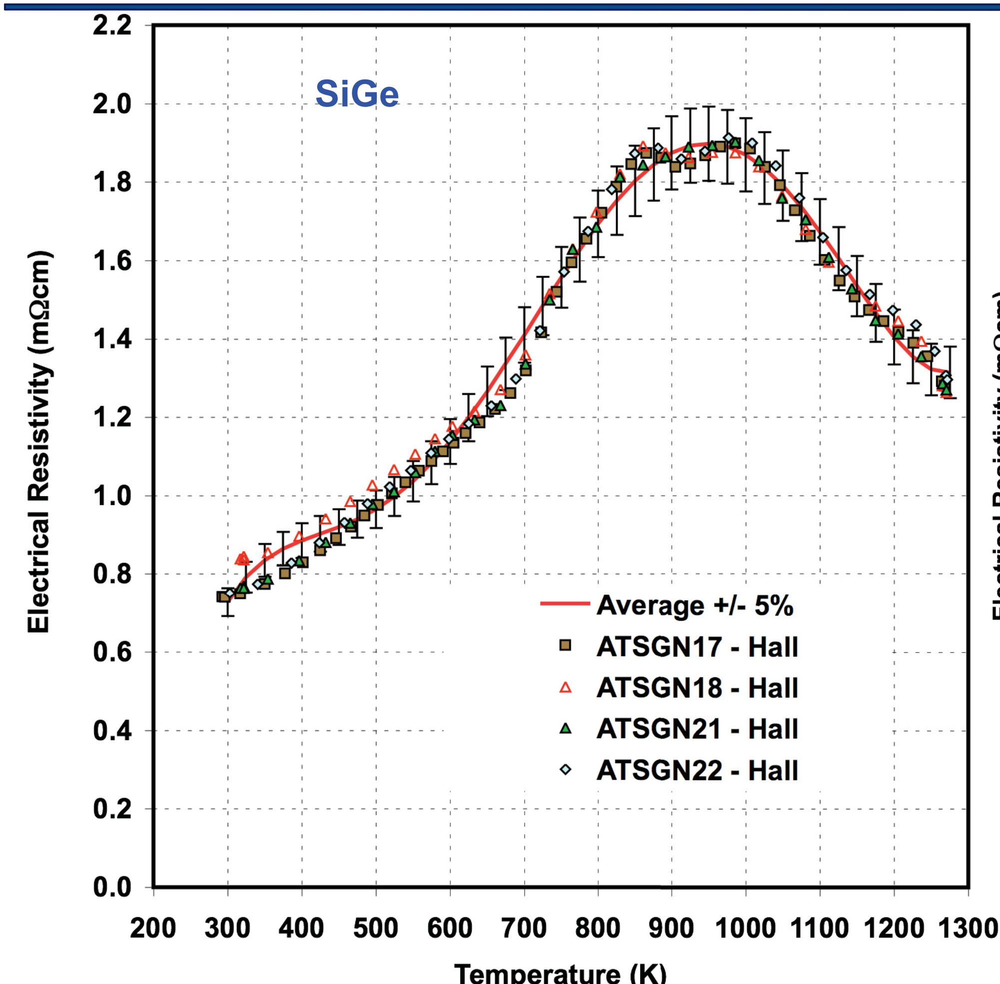
High-temperature Hall effect and van der Pauw measurement system

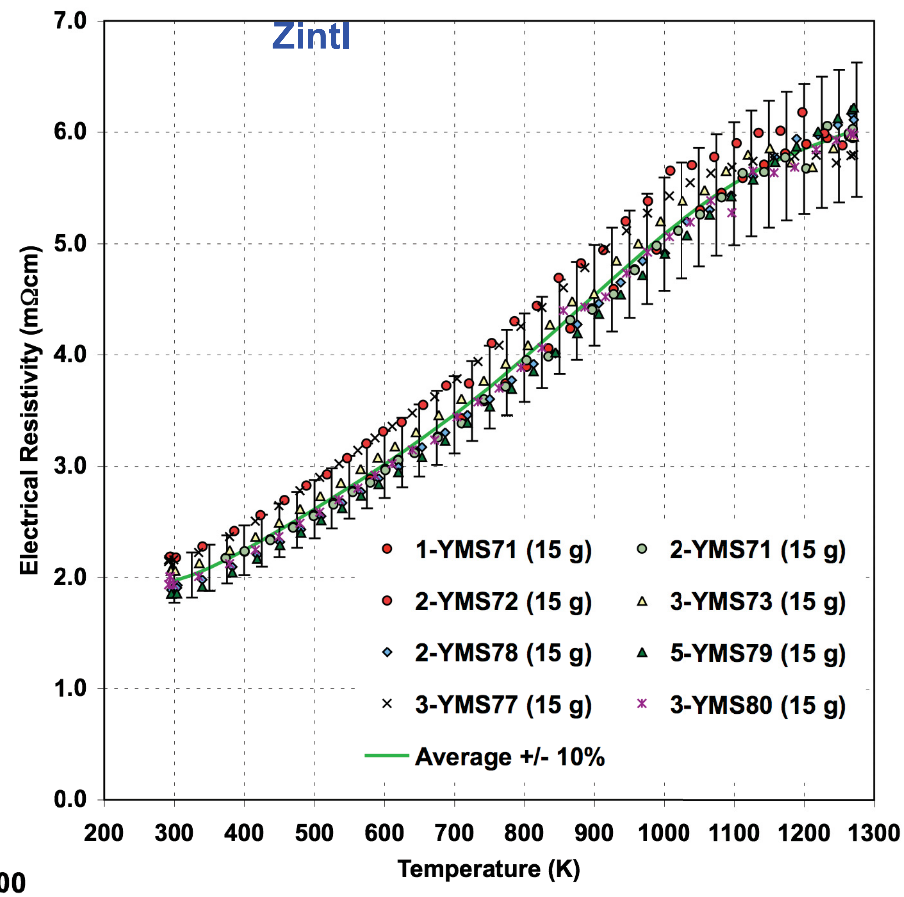
$$ZT \sim \frac{\alpha^2}{\rho\lambda} T$$

Laser flash diffusivity system used for thermal conductivity measurements

- Thermal conductivity (λ) - up to ~ 1375 K
  - Laser flash LFA 457- Diffusivity
  - Heat capacity measured - DSC
  - Use measured geometric density
  - ~ 1 mm thick x 12 mm diameter disk
  - Error ~ 10%

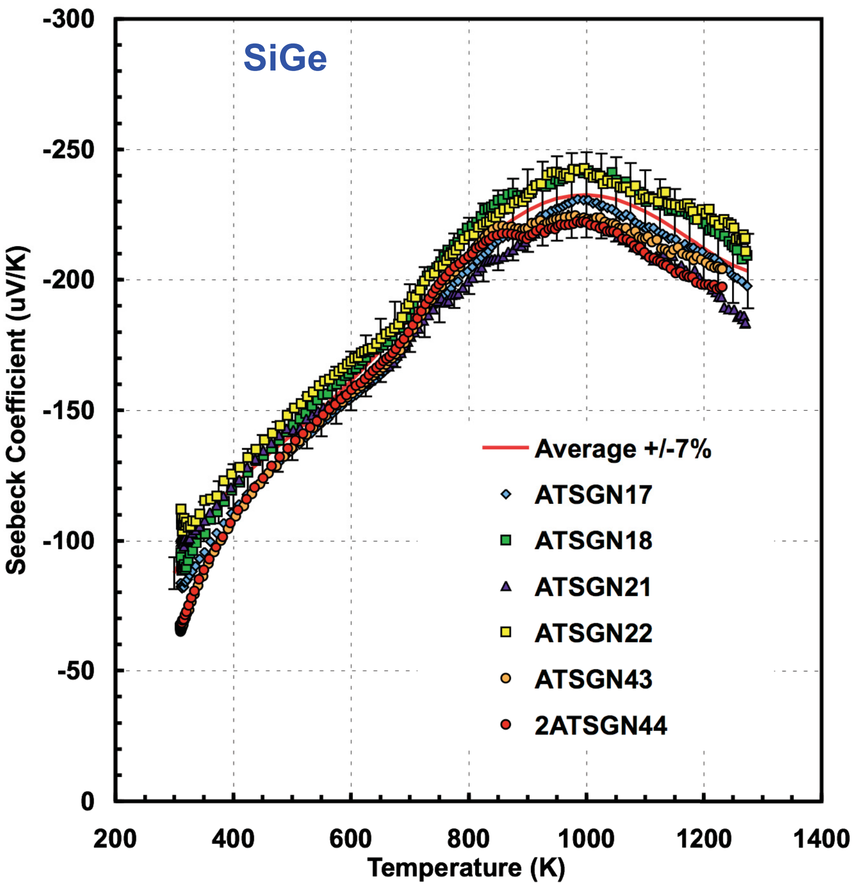
Electrical resistivity (SiGe - Zintl)

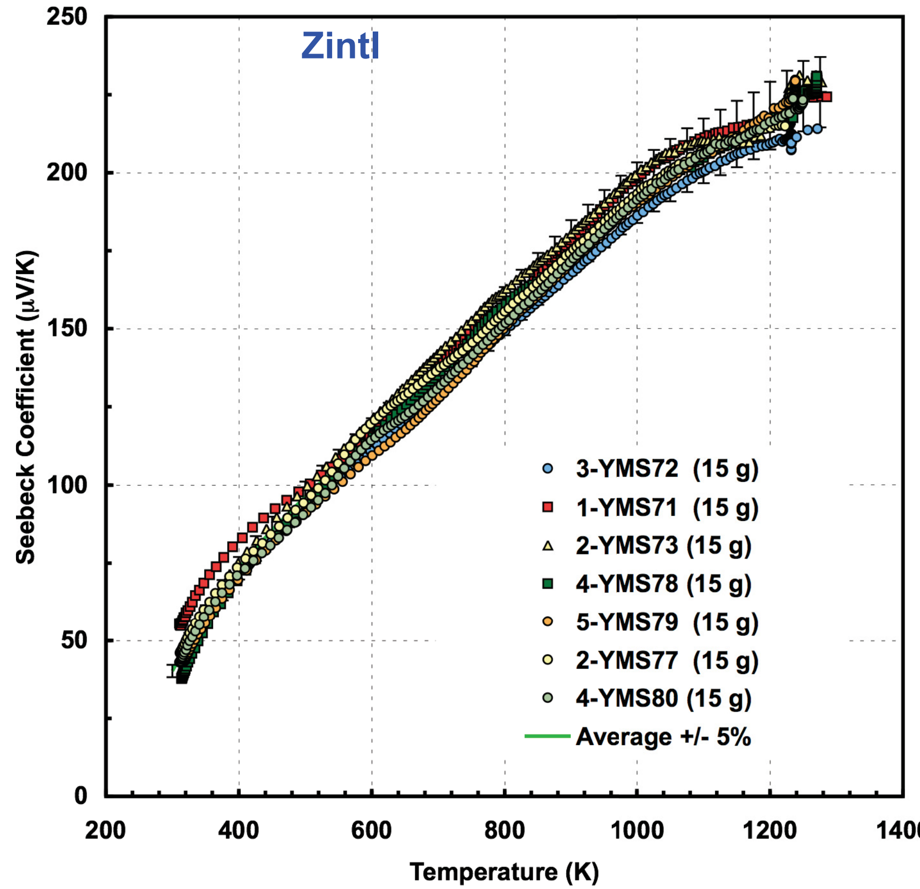




Established repeatability of electrical resistivity for a minimum of four 15 g batches of Zintl and n-MA SiGe

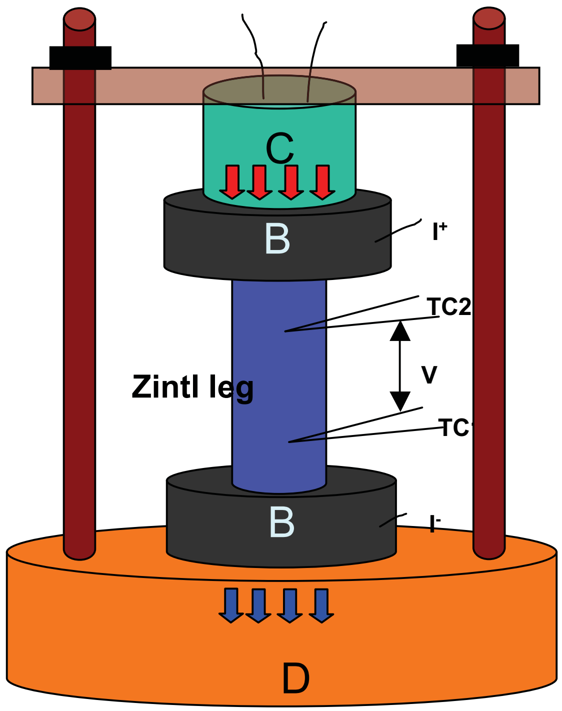
Seebeck coefficient (SiGe- Zintl)

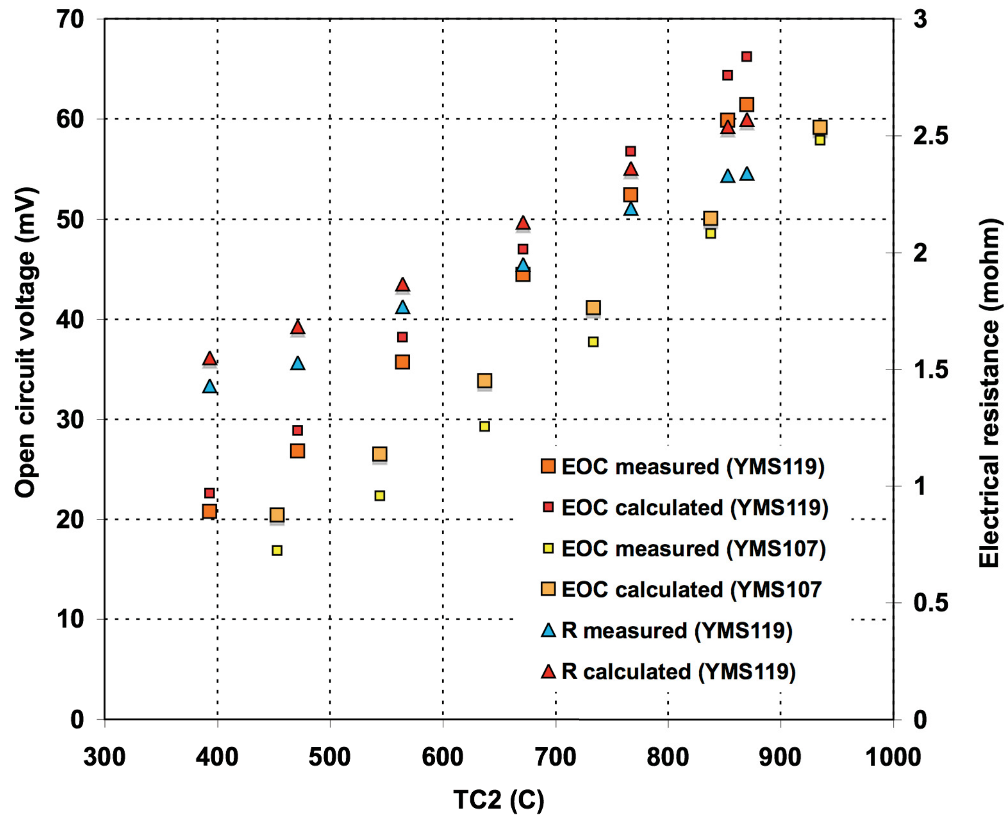




Established repeatability of Seebeck coefficient for a minimum of four 15 g batches of Zintl and n-MA SiGe

Seebeck and resistivity - In-gradient validation

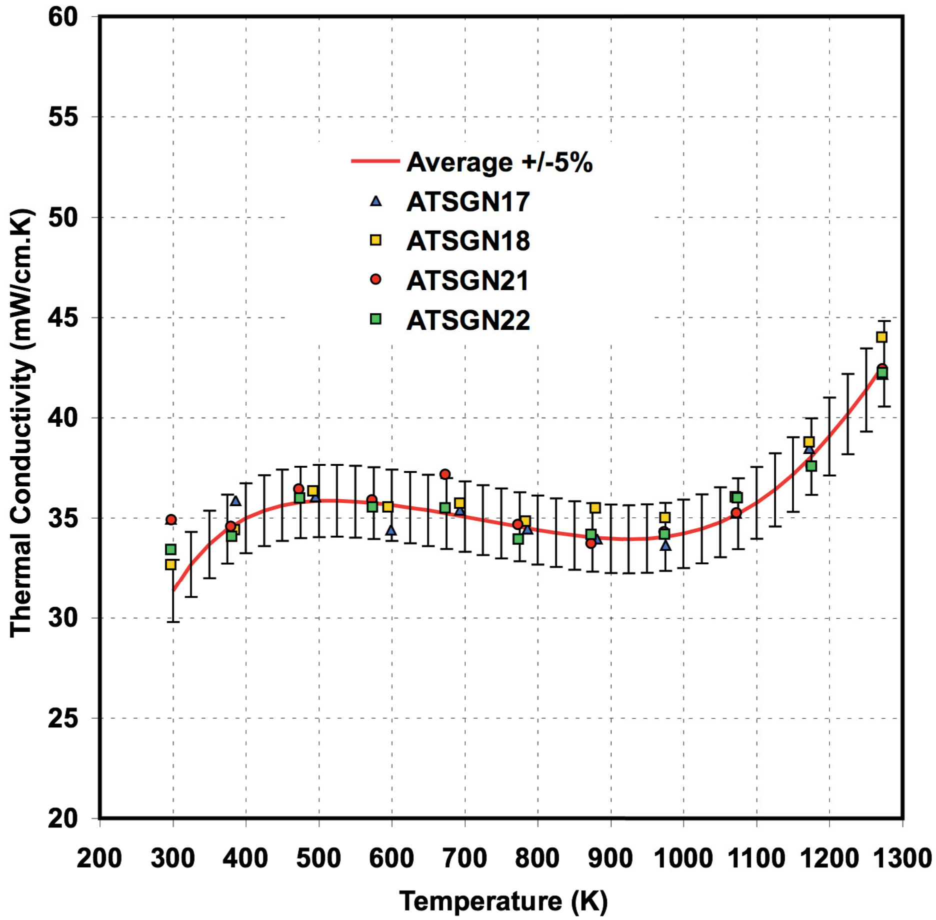




- **In-gradient validation of electrical resistivity and Seebeck coefficient**
  - Zintl leg subjected to large temperature gradient (up to 500 K) in vacuum
  - Measuring voltage and temperature using TC1 and TC2
- **Good agreement between measured voltage and electrical resistance and calculated voltage and resistance from measured Seebeck and electrical resistivity values**

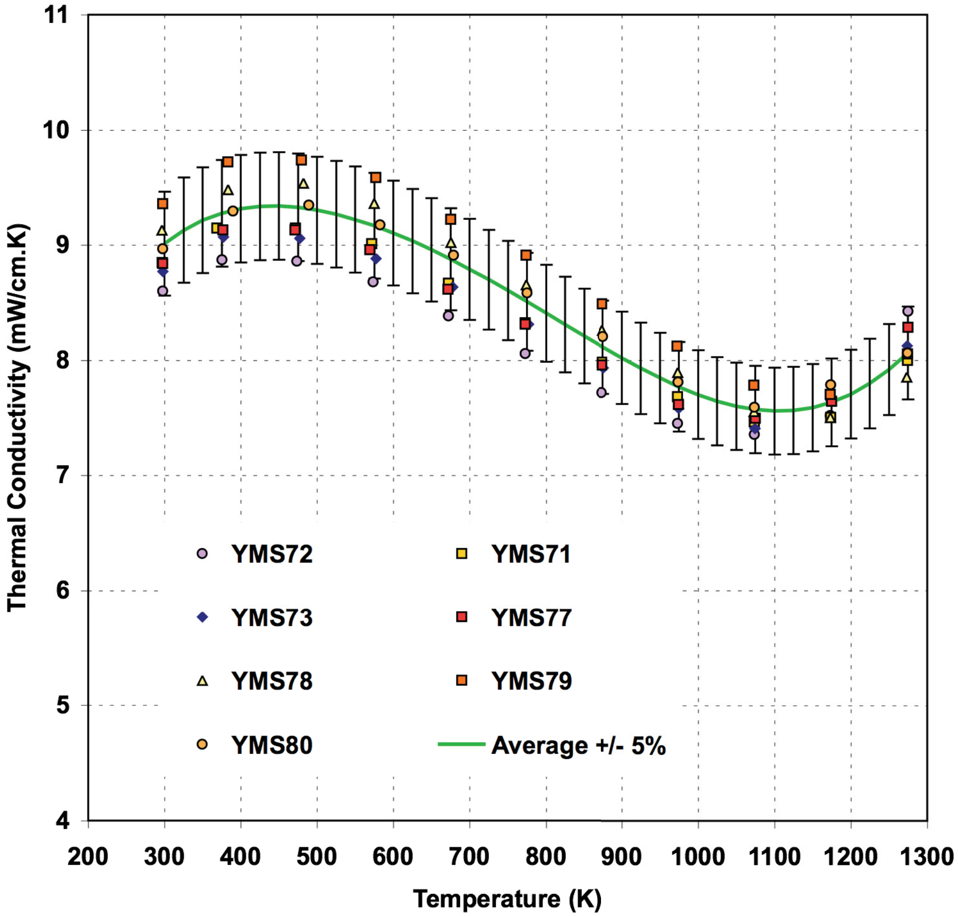
Thermal conductivity (SiGe)

SiGe



Established repeatability of thermal conductivity for a minimum of four 15 g batches of n-MA SiGe

Thermal conductivity (Zintl)

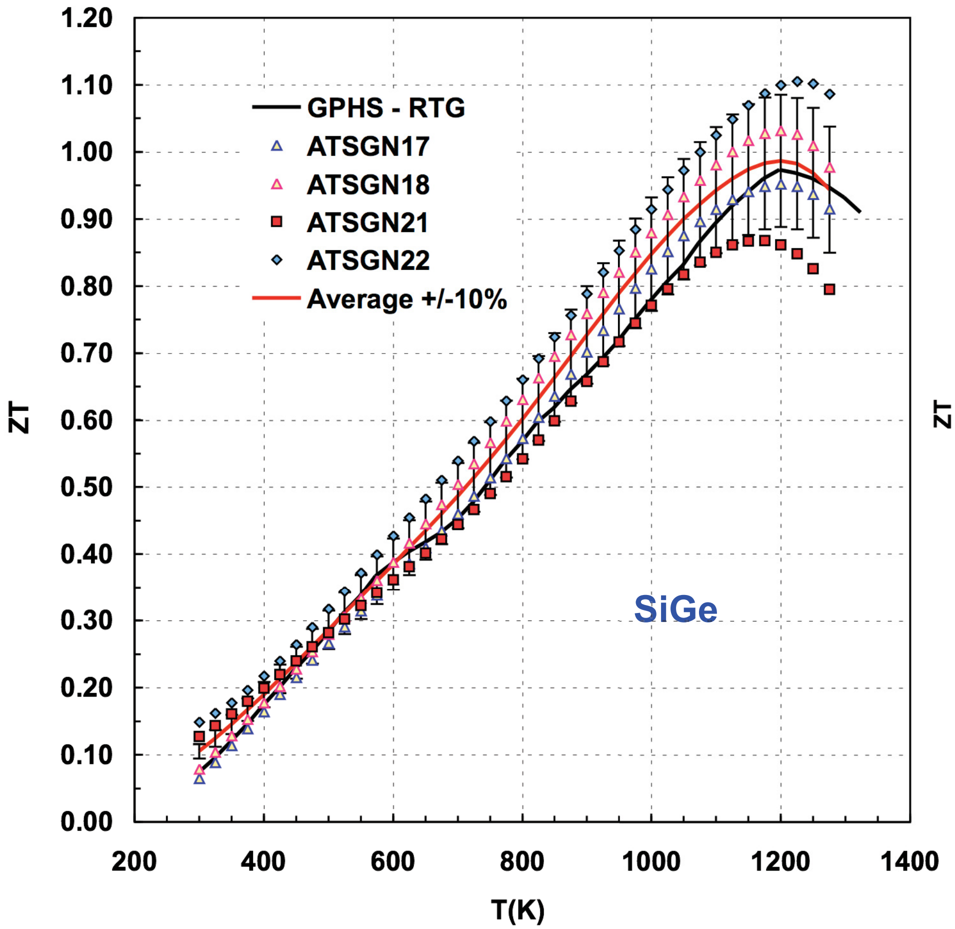


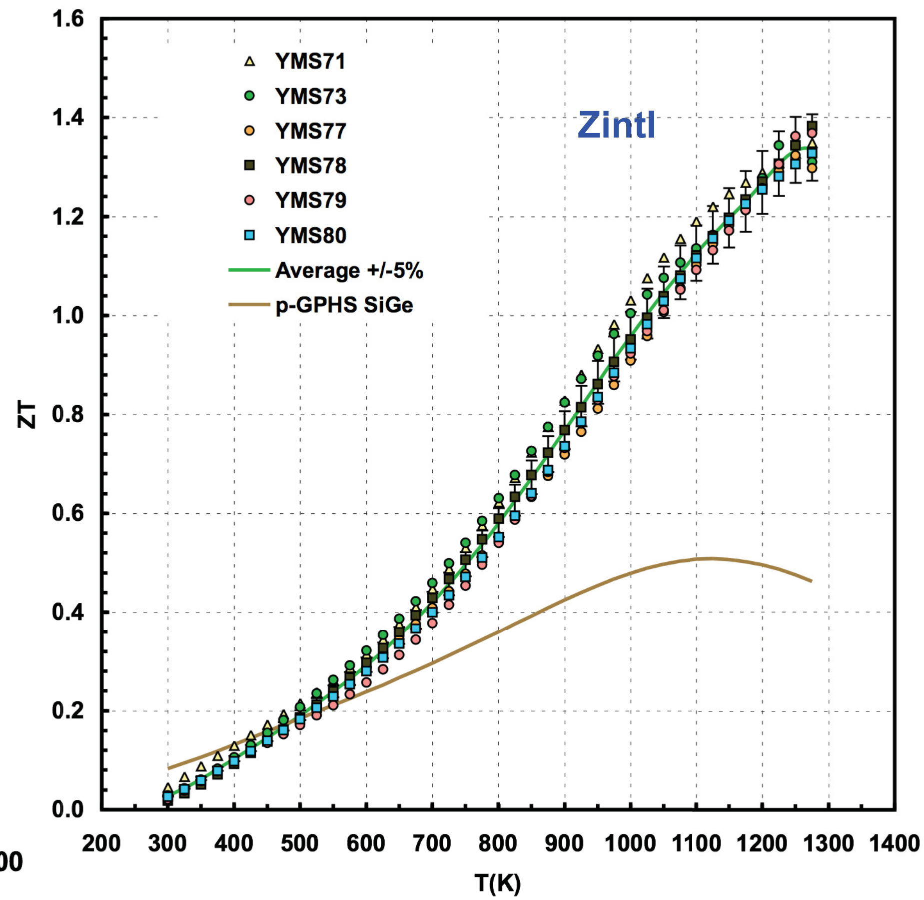
$$\lambda_L = \frac{B\,\bar{M}\delta\theta^2}{q^{2/3}\gamma^2} \qquad \gamma = 3\alpha K V_m / C_v$$

- **Low thermal conductivity**
  - Consistent with previous measurement
- **Calculated lattice thermal conductivity (Wiedemann-Franz)** $\lambda = \lambda_L + L\sigma T$
  - Average value = 6.1 mW/cmK
- **Calculated lattice thermal conductivity (Slack)**
  - 5.1 mW/cmK

- **M= molecular weight**
- **B = 3.04 x 10^7 $s^{-3}K^{-3}$**
- **q = number of atoms per molecule**
- **γ = Grüneisen constant**
- **V_m = averaged sound velocity**
- **α = linear coefficient of expansion**
- **C_v = specific heat capacity per mole**

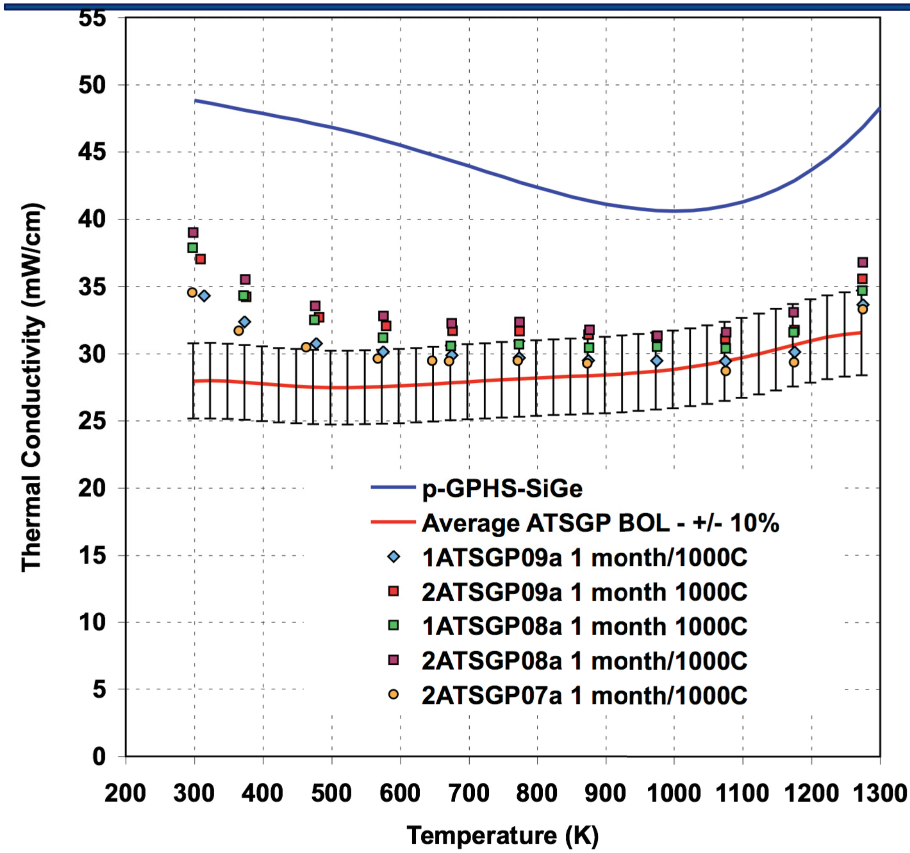
ZT (SiGe- Zintl)

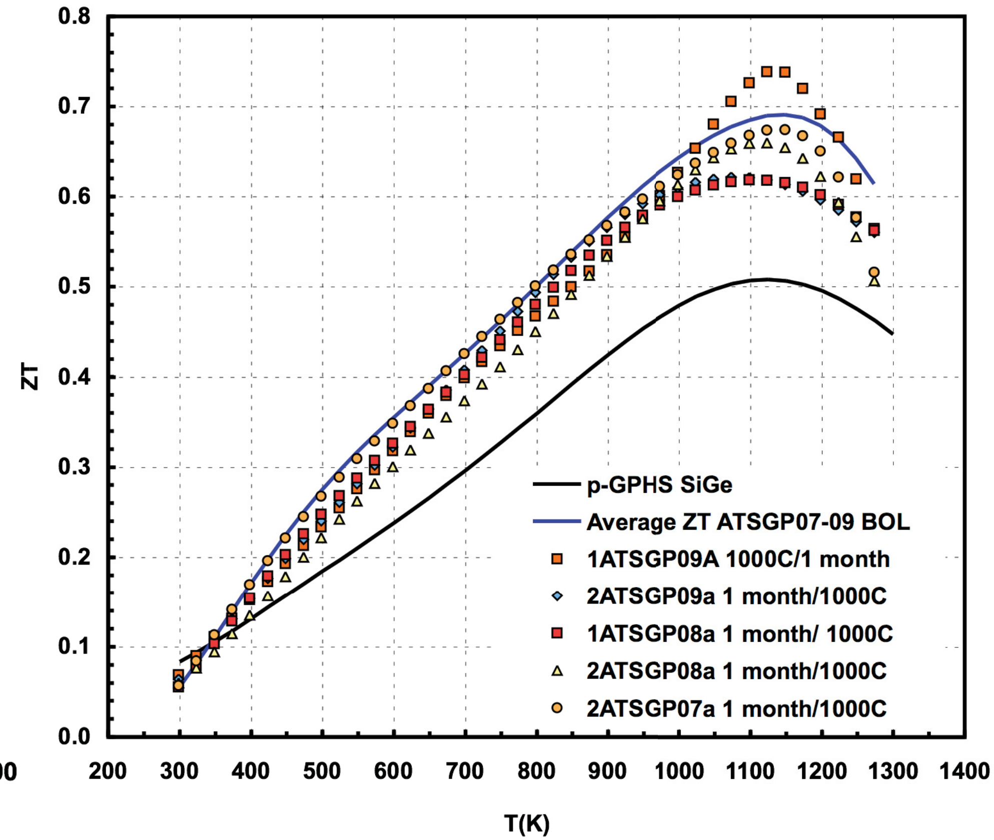




Established repeatability of ZT for a minimum of four 15 g batches of Zintl and n-MA SiGe

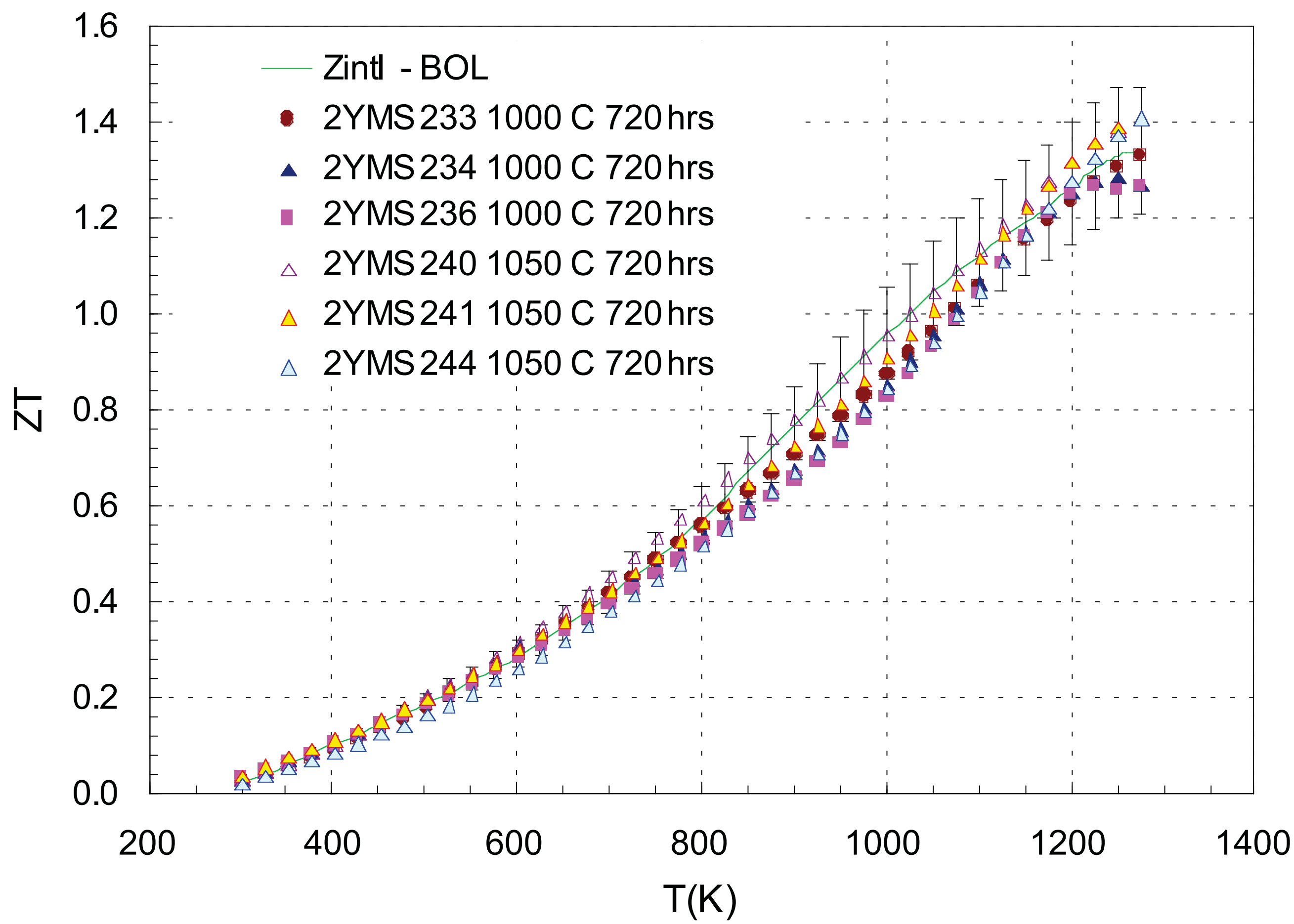
Thermal conductivity and ZT values for p-nano SiGe





- ZT values after 1 month anneal at 1275K show ~ 30% improvement over p-GPHS SiGe
- Relatively small increase in thermal conductivity after anneal

Zintl TE properties life testing

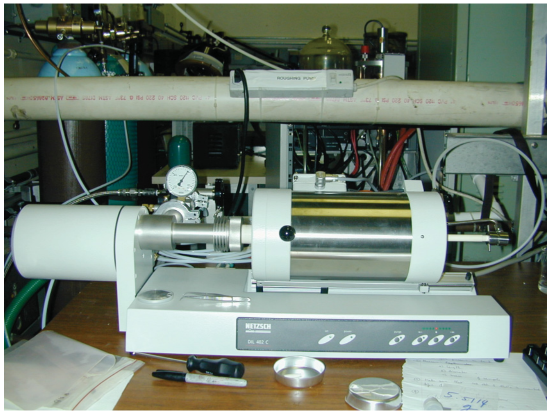


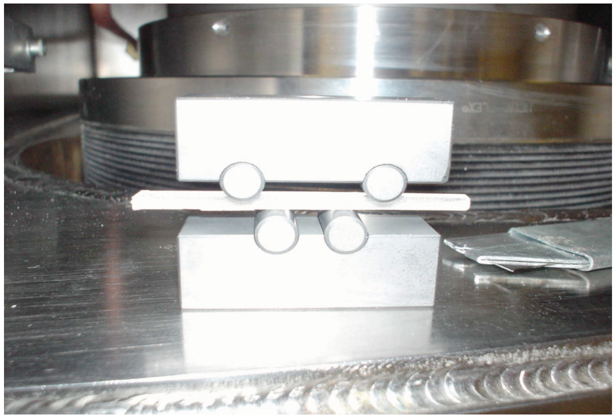
Post anneal ZT values for four different batches are within ± 10% of BOL values

TE materials thermo-mechanical properties

- **Mechanical properties data essential for:**
  - Process development (loading and bonding pressures, etc)
  - Mechanical integrity (handling issues, manufacturing, launch stresses, long-term high temperature performance, residual stresses)

- **Properties of interest**
  - **Stiffness**
    - Elastic Modulii (Young's, shear, bulk, flexural)
    - Poisson's ratio (strain ratio in elastic regime)
  - **Strength**
    - Ultimate load that the material can handle
    - Flexure, compression
  - **Toughness**
    - Resistance to crack propagation - fracture toughness
    - Critical in assessing if the material is susceptible to sudden, brittle fracture (low values of fracture toughness)
  - **Coefficient of thermal expansion**
    - Key in determining mechanical stress state at interfaces of multilayer stack


High-temperature dilatometer


Bend test

Room temperature thermo-mechanical properties

	Melting or Decomposition temperature (K)	Density (g/cm³)	Dynamic Young's Modulus, E (GPa)	Dynamic Shear Modulus, G (GPa)	Poisson's Ratio	Flexural Modulus (GPa)	Flexural Strength (MPa)	Fracture Toughness (MPa-m$^{1/2}$)	Average CTE (ppm/K)
P-SKD	1098	7.92	133	54	0.22 – 0.29	~ 93	~ 37	~ 2.9 *	13.5 (473 – 873 K range)
N-SKD	1049	7.61	136	60	~ 0.14 * 0.25***	~ 102	~ 86	1.6 *	11.0 (473 – 873 K range)
P-Zintl	> 1523	8.36	66***	26***	0.265***	100**	75**	1.0**	17.0 -20.0 (303 – 1273 K range)
$LaTe_{1.43}$	~ 1773	6.68	62***	25***	0.243**	100**	75**	1.0**	17.0 (303 – 1273 K range)
N-SiGe (ATEC)	1573	2.93	145	54**	0.25**	100**	75**	3.3*	5.0 (303 – 1273 K range)
N-SiGe (RTG)	1573	2.99				145	129	~ 0.8	~ 4.9 @ ~ 1200 K ~ 4.7 @ ~ 900 K
P-SiGe (RTG)	1573	2.99				137	201	~ 1	~ 4.8 @ ~ 1200 K ~ 4.6 @ ~ 900 K

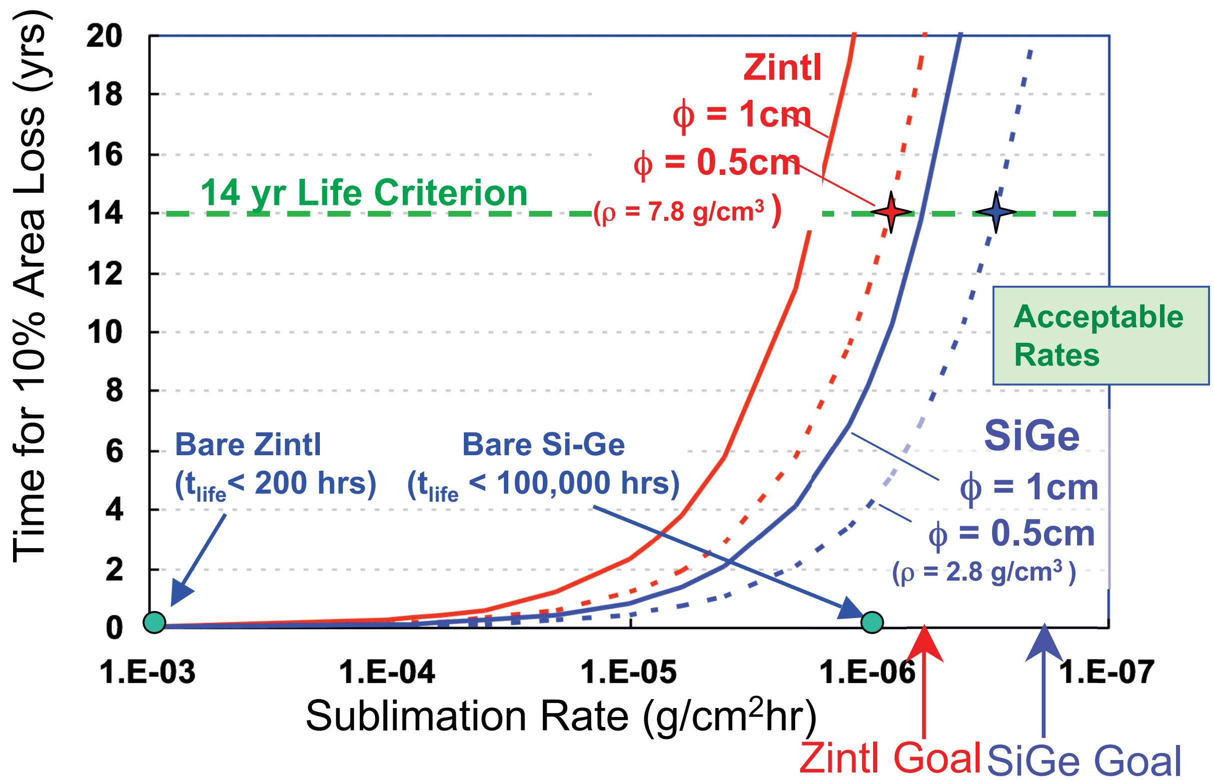
* Preliminary Data ** Estimated (not measured) *** Calculated from speed of sound data

Sublimation Rates

ATEC Sublimation Suppression Requirement:

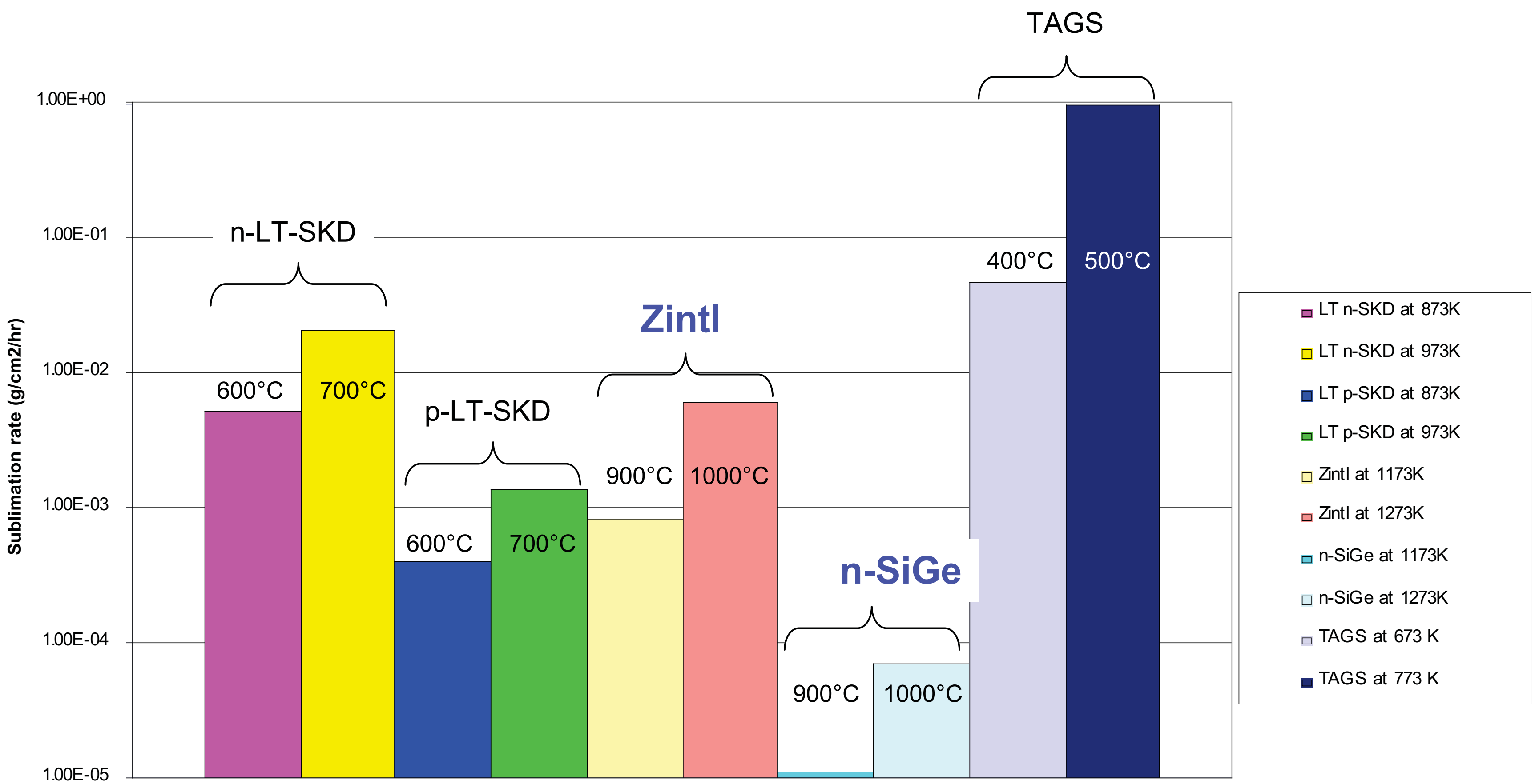
- Less than 10% cross-sectional area lost to sublimation over 14 yrs

Theoretical Predictions of the Time to Lose 10% of the Cross-Sectional Area of a TE Leg



- Sublimation suppression goal for Zintl at 1275 K is ~ 5×10^{-7} g/cm²/hr.
- Sublimation suppression goal for SiGe at 1275 K is ~ 2×10^{-7} g/cm²/hr.

Baseline sublimation rates measured with TGA (2hrs)



Sublimation Control Development

- **Demonstrated sublimation suppression of LT-SKD with aerogel (~ 5 × 10^{-7} g/cm^{2}h at 875 K for 6000 hrs).**

- **Identified candidates for Zintl sublimation suppression.**
  - **Ceramic cements (~100μm) (Rate ~ 5 × 10^{-6} g/cm^2/hr, 4 wks at 1275 K).**
  - **Physical barrier (no measurable sublimation during in-gradient test of Zintl leg, 1 wk at 1275 K).**
  - **Thin metal coatings, semi-protective after 2 wks at 1275 K.**

- **Identified candidates for SiGe sublimation suppression.**
  - **Graphite aerogel (Rate ~ 8.5 × 10^{-7} g/cm^2/hr after 2 weeks at 1275 K).**
  - **Si_3N_4**

Summary

- **NASA and DOE are working together to develop a next generation RTG that would provide significant benefits for future NASA deep space missions**
  – Higher payload mass/reduced power system mass
  – Lower launch vehicle costs
  – Reduced plutonium usage
  – High reliability and long life capability

- **Significant progress has been made in the area of materials and component development, and system design**
  – Demonstrated material reproducibility, scalability and initial TE property stability
  – > 6W/kg and > 8% system efficiency
  – Zintl / SiGe unicouples selected

- **JPL developing the next generation of advanced materials that could lead to advanced RTGs capable of up to 17% system efficiency and over 12 W/kg specific power**
  – High temperature Zintls / rare earth chalcogenides with average ZT ~ 2
  – Nanostructured materials engineering of high power factor Si, Ge and III-V electronic semiconductors (1275 K – 500 K)